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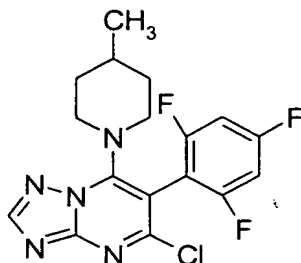
Fungicidal mixtures for controlling rice pathogens.

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The present invention relates to fungicidal mixtures for controlling rice pathogens,  
which mixtures comprise, as active components,

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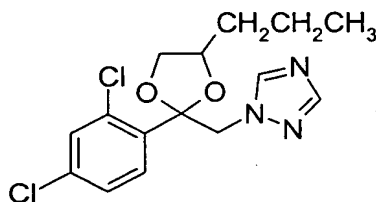
- 1) the triazolopyrimidine derivative of the formula I,



I

and

- 10 2) propiconazole of the formula II,



II

in a synergistically effective amount.

- 15 Moreover, the invention relates to a method for controlling rice pathogens using mixtures of the compound I with the compound II and to the use of the compound I with the compound II for preparing such mixtures and compositions comprising these mixtures.

- 20 The compound I, 5-chloro-7-(4-methylpiperidin-1-yl)-6-(2,4,6-trifluorophenyl)-[1,2,4]triazolo[1,5-a]pyrimidine, its preparation and its action against harmful fungi are known from the literature (WO 98/46607).

- 25 The compound II, 1-[2-(2,4-dichlorophenyl)-4-propyl-[1,3]dioxolan-2-ylmethyl]-1H-[1,2,4]triazole, its preparation and its action against harmful fungi are likewise known from the literature (Proc. Br. Crop Prot. Conf., 1979, Vol. 2, p.508; GB 15 22657; common name propiconazole).

- 30 Mixtures of triazolopyrimidine derivatives with propiconazole are known in a general manner from EP-A 988 790. The compound I is embraced by the general disclosure of

this publication, but not explicitly mentioned. Accordingly, the combination of compound I with propiconazole is novel.

The synergistic mixtures known from EP-A 988 790 are described as being fungicidally active against various diseases of cereals, fruit and vegetables, for example mildew on wheat and barley or gray mold on apples.

It was an object of the present invention to provide, with a view to effective control of rice pathogens at application rates which are as low as possible, mixtures which, at a reduced total amount of active compounds applied, have improved action against the rice pathogens.

Owing to the special cultivation conditions of rice plants, the requirements that a rice fungicide has to meet are considerably different from those that fungicides used in cereal or fruit growing have to meet. There are differences in the application method: in modern rice cultivation, in addition to foliar application, which is used in many places, the fungicide is applied directly onto the soil during or shortly after sowing. The fungicide is taken up into the plant via the roots and transported in the sap of the plant to the plant parts to be protected. The systemic action of the active compounds is considerably less important.

Moreover, rice pathogens are typically different from those in cereal or fruit. *Pyricularia oryzae* and *Corticium solani* (syn. *Rhizoctonia sasakii*) are the pathogens of the diseases most prevalent in rice plants. *Rhizoctonia sasakii* is the only pathogen of agricultural significance from the sub-class *Agaricomycetidae*. In contrast to most other fungi, this fungus attacks the plants not via spores but via a mycelium infection.

For this reason, findings concerning the fungicidal activity in the cultivation of cereals or fruit cannot be transferred to rice crops.

It was an object of the present invention to provide, with a view to effective control of rice pathogens at application rates which are as low as possible, mixtures which, at a reduced total amount of active compounds applied, have improved action against the harmful fungi (synergistic mixtures).

We have found that this object is achieved by the mixtures defined at the outset. Surprisingly, it has been found that the propiconazole mixtures defined at the outset allow considerably better control of rice pathogens than the propiconazole mixtures, disclosed in EP-A 988 790 of the triazolopyrimidine compounds. Moreover, we have found that simultaneous, that is joint or separate, application of the compound I and the

compound II or successive application of the compound I and the compound II allows better control of rice pathogens than is possible with the individual compounds.

- 5 When preparing the mixtures, it is preferred to employ the pure active compounds I and II, to which further active compounds against harmful fungi or other pests, such as insects, arachnids or nematodes, or else herbicidal or growth-regulating active compounds or fertilizers can be added as required.

10 Other suitable fungicides in the above sense are in particular fungicides selected from the following group:

- acylalanines, such as benalaxyl, ofurace, oxadixyl,
- amine derivatives, such as aldimorph, dodemorph, fenpropidin, guazatine, iminoctadine, tridemorph,
- 15 • anilinopyrimidines, such as pyrimethanil, mepanipyrim or cyprodinyl,
- antibiotics, such as cycloheximide, griseofulvin, kasugamycin, natamycin, polyoxin or streptomycin,
- azoles, such as bitertanol, bromoconazole, cyproconazole, difenoconazole, dinitroconazole, enilconazole, fenbuconazole, fluquinconazole, flusilazole, flutriafol,
- 20 • hexaconazole, imazalil, ipconazole, myclobutanil, penconazole, prochloraz, prothioconazole, simeconazole, tetraconazole, triadimefon, triadimenol, triflumizole, triticonazole,
- dicarboximides, such as myclozolin, procymidone,
- dithiocarbamates, such as ferbam, nabam, metam, propineb, polycarbamate, ziram
- 25 or zineb,
- heterocyclic compounds, such as anilazine, boscalid, oxycarboxin, cyazofamid, dazomet, famoxadone, fenamidone, fuberidazole, flutolanil, furametpyr, isoprothiolane, mepronil, nuarimol, probenazole, pyroquilon, silthiofam, thiabendazole, thifluzamide, tiadinil, tricyclazole, triforine,
- 30 • nitrophenyl derivatives, such as binapacryl, dinocap, dinobuton, nitrophthal-isopropyl,
- other fungicides, such as acibenzolar-S-methyl, carpropamid, chlorothalonil, cyflufenamid, cymoxanil, diclomezine, diclocymet, diethofencarb, edifenphos, ethaboxam, fentin-acetate, fenoxanil, ferimzone, fosetyl, hexachlorobenzene, metrafenone, pencycuron, propamocarb, phthalide, tolclofos-methyl, quintozone,
- 35 zoxamide,
- strobilurins, such as fluoxastrobin, metominostrobin, orysastrobin or pyraclostrobin,
- sulfenic acid derivatives, such as captafol,
- cinnamides and analogous compounds, such as flumetover.

In one embodiment of the mixtures according to the invention, a further fungicide III or two fungicides III and IV are added to the compounds I and II. Preference is given to mixtures of the compounds I and II with a component III. Particular preference is given to mixtures of the compounds I and II.

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The mixtures of compounds I and II, or the compound I and the compound II used simultaneously, that is jointly or separately, exhibit outstanding action against rice pathogens from the classes of the *Ascomycetes*, *Deuteromycetes* and *Basidiomycetes*. They can be used for the treatment of seed and as foliar- and soil-acting fungicides.

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They are especially important for controlling harmful fungi on rice plants and their seeds, such as *Bipolaris* and *Drechslera* species, and also *Pyricularia oryzae*. They are particularly suitable for controlling rice blast caused by *Pyricularia oryzae*.

15

In addition, the combination according to the invention of the compounds I and II can also be used for controlling other pathogens, such as, for example, *Septoria* and *Puccinia* species in cereals and *Alternaria* and *Botrytis* species in vegetables, fruit and grapevines.

20

The combinations according to the invention are furthermore suitable for controlling harmful fungi such as *Paecilomyces variotii* in the protection of materials (for example wood, paper, paint dispersions, fibers and/or fabric) and in the protection of stored products.

25

The compound I and the compound II can be applied simultaneously, that is jointly or separately, or in succession, the sequence, in the case of separate application, generally not having any effect on the result of the control measures.

30

The compound I and the compound II are usually applied in a weight ratio of from 100:1 to 1:100, preferably from 20:1 to 1:20, in particular from 10:1 to 1:10.

The components III and, if appropriate, IV are added, if desired, to the compound I in a ratio of from 20:1 to 1:20.

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Depending on the type of compound and on the desired effect, the application rates of the mixtures according to the invention are from 5 g/ha to 2000 g/ha, preferably from 50 to 1500 g/ha, in particular from 50 to 750 g/ha.

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Correspondingly, the application rates of the compound I are generally from 1 to 1000 g/ha, preferably from 10 to 900 g/ha, in particular from 20 to 750 g/ha.

Correspondingly, the application rates of the compound II are generally from 1 to 1000 g/ha, preferably from 10 to 750 g/ha, in particular from 20 to 500 g/ha.

- 5 In the treatment of seed, the application rates of mixture are generally from 1 to 1000 g/100 kg of seed, preferably from 1 to 200 g/100 kg, in particular from 5 to 100 g/100 kg.

- 10 When used in the protection of materials or stored products, the amount of active compound applied depends on the kind of application area and on the desired effect. Amounts customarily applied in the protection of materials are, for example, 0.0001 g to 2 kg, preferably 0.005 g to 1 kg, of mixtures according to the invention per cubic meter of treated material. The application in the protection of wood is preferred.

- 15 In the control of harmful fungi pathogenic to plants, the separate or joint application of the compounds I and II or of the mixtures of the compounds I and II is carried out by spraying or dusting the seeds, the seedlings, the plants or the soils before or after sowing of the plants or before or after emergence of the plants. The compounds are preferably applied jointly or separately by applying granules or by dusting the soils. The  
20 compounds are particularly preferably applied jointly or separately by spraying the leaves.

- The mixtures according to the invention or the compounds I and II can be converted into the customary formulations, for example solutions, emulsions, suspensions, dusts,  
25 powders, pastes and granules. The application form depends on the particular purpose; in each case, it should ensure a fine and uniform distribution of the compound according to the invention.

- The formulations are prepared in a known manner, for example by extending the active  
30 compound with solvents and/or carriers, if desired using emulsifiers and dispersants. Solvents/auxiliaries which are suitable are essentially:

- water, aromatic solvents (for example Solvesso products, xylene), paraffins (for example mineral oil fractions), alcohols (for example methanol, butanol, pentanol, benzyl alcohol), ketones (for example cyclohexanone, gamma-  
35 butyrolactone), pyrrolidones (NMP, NOP), acetates (glycol diacetate), glycols, fatty acid dimethylamides, fatty acids and fatty acid esters. In principle, solvent mixtures may also be used.
- carriers such as ground natural minerals (for example kaolins, clays, talc, chalk) and ground synthetic minerals (for example highly disperse silica, silicates);  
40 emulsifiers such as nonionic and anionic emulsifiers (for example

polyoxyethylene fatty alcohol ethers, alkylsulfonates and arylsulfonates) and dispersants such as lignosulfite waste liquors and methylcellulose.

Suitable surfactants are alkali metal, alkaline earth metal and ammonium salts of  
5 lignosulfonic acid, naphthalenesulfonic acid, phenolsulfonic acid,  
dibutyl naphthalenesulfonic acid, alkylarylsulfonates, alkyl sulfates, alkylsulfonates, fatty  
alcohol sulfates, fatty acids and sulfated fatty alcohol glycol ethers, furthermore  
condensates of sulfonated naphthalene and naphthalene derivatives with  
formaldehyde, condensates of naphthalene or of naphthalenesulfonic acid with phenol  
10 and formaldehyde, polyoxyethylene octylphenyl ether, ethoxylated isooctylphenol,  
octylphenol, nonylphenol, alkylphenyl polyglycol ethers, tributylphenyl polyglycol ether,  
tristearylphenyl polyglycol ether, alkylaryl polyether alcohols, alcohol and fatty alcohol  
ethylene oxide condensates, ethoxylated castor oil, polyoxyethylene alkyl ethers,  
ethoxylated polyoxypropylene, lauryl alcohol polyglycol ether acetal, sorbitol esters,  
15 lignosulfite waste liquors and methylcellulose.

Substances which are suitable for the preparation of directly sprayable solutions,  
emulsions, pastes or oil dispersions are mineral oil fractions of medium to high boiling  
point, such as kerosene or diesel oil, furthermore coal tar oils and oils of vegetable or  
20 animal origin, aliphatic, cyclic and aromatic hydrocarbons, for example toluene, xylene,  
paraffin, tetrahydronaphthalene, alkylated naphthalenes or their derivatives, methanol,  
ethanol, propanol, butanol, cyclohexanol, cyclohexanone, isophorone, strongly polar  
solvents, for example dimethyl sulfoxide, N-methylpyrrolidone and water.

25 Powders, materials for spreading and dustable products can be prepared by mixing or  
concomitantly grinding the active substances with a solid carrier.

Granules, for example coated granules, impregnated granules and homogeneous  
granules, can be prepared by binding the active compounds to solid carriers. Examples  
30 of solid carriers are mineral earths such as silica gels, silicates, talc, kaolin, attaclay,  
limestone, lime, chalk, bole, loess, clay, dolomite, diatomaceous earth, calcium sulfate,  
magnesium sulfate, magnesium oxide, ground synthetic materials, fertilizers, such as,  
for example, ammonium sulfate, ammonium phosphate, ammonium nitrate, ureas, and  
products of vegetable origin, such as cereal meal, tree bark meal, wood meal and  
35 nutshell meal, cellulose powders and other solid carriers.

In general, the formulations comprise from 0.01 to 95% by weight, preferably from 0.1  
to 90% by weight, of the active compounds. The active compounds are employed in a  
purity of from 90% to 100%, preferably 95% to 100% (according to NMR spectrum).

The following are examples of formulations: 1. Products for dilution with water

A) Water-soluble concentrates (SL)

10 parts by weight of the active compounds are dissolved in water or in a water-soluble solvent. As an alternative, wetters or other auxiliaries are added. The active compound dissolves upon dilution with water.

B) Dispersible concentrates (DC)

20 parts by weight of the active compounds are dissolved in cyclohexanone with addition of a dispersant, for example polyvinylpyrrolidone. Dilution with water gives a dispersion.

C) Emulsifiable concentrates (EC)

15 parts by weight of the active compounds are dissolved in xylene with addition of calcium dodecylbenzenesulfonate and castor oil ethoxylate (in each case 5% strength). Dilution with water gives an emulsion.

D) Emulsions (EW, EO)

40 parts by weight of the active compounds are dissolved in xylene with addition of calcium dodecylbenzenesulfonate and castor oil ethoxylate (in each case 5% strength). This mixture is introduced into water by means of an emulsifying machine (Ultraturrax) and made into a homogeneous emulsion. Dilution with water gives an emulsion.

E) Suspensions (SC, OD)

In an agitated ball mill, 20 parts by weight of the active compounds are comminuted with addition of dispersants, wetters and water or an organic solvent to give a fine active compound suspension. Dilution with water gives a stable suspension of the active compound.

F) Water-dispersible granules and water-soluble granules (WG, SG)

50 parts by weight of the active compounds are ground finely with addition of dispersants and wetters and made into water-dispersible or water-soluble granules by means of technical appliances (for example extrusion, spray tower, fluidized bed). Dilution with water gives a stable dispersion or solution of the active compound.

G) Water-dispersible powders and water-soluble powders (WP, SP)

75 parts by weight of the active compounds are ground in a rotor-stator mill with addition of dispersants, wetters and silica gel. Dilution with water gives a stable dispersion or solution of the active compound.

## 2. Products to be applied undiluted

## H) Dustable powders (DP)

5 parts by weight of the active compounds are ground finely and mixed intimately with 95% of finely divided kaolin. This gives a dustable product.

## I) Granules (GR, FG, GG, MG)

0.5 part by weight of the active compounds is ground finely and associated with 95.5% carriers. Current methods are extrusion, spray-drying or the fluidized bed. This gives granules to be applied undiluted.

## J) ULV solutions (UL)

10 parts by weight of the active compounds are dissolved in an organic solvent, for example xylene. This gives a product to be applied undiluted.

The active compounds can be used as such, in the form of their formulations or the use forms prepared therefrom, for example in the form of directly sprayable solutions, powders, suspensions or dispersions, emulsions, oil dispersions, pastes, dustable products, materials for spreading, or granules, by means of spraying, atomizing, dusting, spreading or pouring. The use forms depend entirely on the intended purposes; they are intended to ensure in each case the finest possible distribution of the active compounds according to the invention.

Aqueous use forms can be prepared from emulsion concentrates, pastes or wettable powders (sprayable powders, oil dispersions) by adding water. To prepare emulsions, pastes or oil dispersions, the substances, as such or dissolved in an oil or solvent, can be homogenized in water by means of a wetter, tackifier, dispersant or emulsifier. Alternatively, it is possible to prepare concentrates composed of active substance, wetter, tackifier, dispersant or emulsifier and, if appropriate, solvent or oil, and such concentrates are suitable for dilution with water.

The active compound concentrations in the ready-to-use preparations can be varied within relatively wide ranges. In general, they are from 0.0001 to 10%, preferably from 0.01 to 1%.

The active compounds may also be used successfully in the ultra-low-volume process (ULV), it being possible to apply formulations comprising over 95% by weight of active compound, or even to apply the active compound without additives.

Oils and various types, wetters, adjuvants, herbicides, fungicides, other pesticides, or



bactericides may be added to the active compounds, if appropriate just immediately prior to use (tank mix). These agents can be admixed with the agents according to the invention, typically in a weight ratio of 1:10 to 10:1.

- 5 The compounds I and II or the mixtures or the corresponding formulations are applied by treating the harmful fungi or the plants, seeds, soils, areas, materials or spaces to be kept free from them with a fungicidally effective amount of the mixture or, in the case of separate application, of the compounds I and II. Application can be carried out before or after infection by the harmful fungi.

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The fungicidal action of the compound and the mixtures can be demonstrated by the experiments below:

- 15 The active compounds, separately or jointly, were prepared as a stock solution with 0.25% by weight of active compound in acetone or DMSO. 1% by weight of the emulsifier Uniperol® EL (wetting agent having emulsifying and dispersing action based on ethoxylated alkylphenols) was added to this solution, and the solution was diluted with water to the desired concentration.

- 20 Use example – protective activity against rice blast caused by *Pyricularia oryzae*

- Leaves of rice seedlings of the cultivar "Tai-Nong 67", which had been grown in pots, were sprayed to runoff point with an aqueous suspension having the concentration of active compounds stated below. The next day, the plants were inoculated with an aqueous spore suspension of *Pyricularia oryzae*. The test plants were then placed in climatized chambers at 22-24°C and 95-99% relative atmospheric humidity for 6 days. The extent of the development of the infection on the leaves was then determined visually.

- 30 Evaluation was carried out by determining the infected leaf areas in percent. These percentages were converted into efficacies.

The efficacy (E) is calculated as follows using Abbot's formula:

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$$E = (1 - \alpha/\beta) \cdot 100$$

$\alpha$  corresponds to the fungicidal infection of the treated plants in % and

$\beta$  corresponds to the fungicidal infection of the untreated (control) plants in %

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An efficacy of 0 means that the infection level of the treated plants corresponds to that of the untreated control plants; an efficacy of 100 means that the treated plants are not infected.

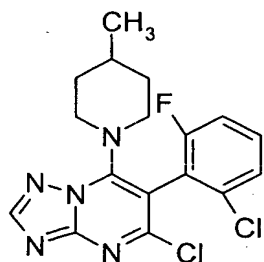
- 5 The expected efficacies of mixtures of active compounds are determined using Colby's formula (Colby, R.S., Weeds, 15, 20-22, 1967) and compared with the observed efficacies.

Colby's formula:

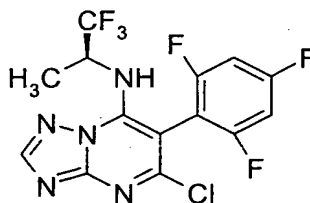
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$$E = x + y - x \cdot y / 100$$

- E expected efficacy, expressed in % of the untreated control, when using the mixture of the active compounds A and B at the concentrations a and b
- 15 x efficacy, expressed in % of the untreated control, when using the active compound A at the concentration a
- y efficacy, expressed in % of the untreated control, when using the active compound B at the concentration b
- 20 The comparative compounds used were compounds A and B which are known from the propiconazole mixtures described in EP-A 988 790:



A



B

Table A - individual active compounds

Ex-ample	Active compound	Concentration of active compound in the spray liquor [ppm]	Efficacy in % of the untreated control
1	Control (untreated)	-	(90 % infection)
2	I	4	33
		1	11
3	II (propiconazole)	4	0
		1	0
4	comparative compound A	4	11
		1	0

Ex-ample	Active compound	Concentration of active compound in the spray liquor [ppm]	Efficacy in % of the untreated control
5	comparative compound	4	33
	B	1	11

Table B – mixtures according to the invention

Ex-ample	Mixture of active compounds Concentration Mixing ratio	Observed efficacy	Calculated efficacy*)
6	I + II	67	33
	4 + 1 ppm 4:1		
7	I + II	78	33
	4 + 4 ppm 1:1		
8	I + IIa	67	11
	1 + 4 ppm 1:4		

\*) efficacy calculated using Colby's formula

## 5 Table C – comparative tests

Propiconazole mixtures known from EP-A 988 780

Ex-ample	Mixture of active compounds Concentration Mixing ratio	Observed efficacy	Calculated efficacy*)
9	A + II	33	11
	4 + 1 ppm 4:1		
10	A + II	44	11
	4 + 4 ppm 1:1		
11	A + II	33	0
	1 + 4 ppm 1:4		
12	B + II	44	33
	4 + 1 ppm 4:1		

Ex-ample	Mixture of active compounds Concentration Mixing ratio	Observed efficacy	Calculated efficacy*)
13	B + II 4 + 4 ppm 1:1	44	33
14	B + II 1 + 4 ppm 1:4	33	11

\*) efficacy calculated using Colby's formula

- 5 The test results show that the mixtures according to the invention, by virtue of strong synergism, are considerably more effective against rice blast than the propiconazole mixtures, known from EP-A 988 780, of the comparative compounds, although the individual compounds are comparatively effective.